

## PATENT ABSTRACTS OF JAPAN

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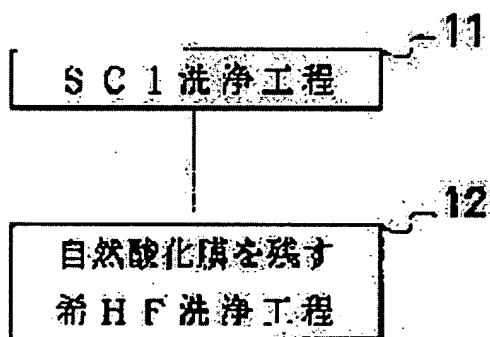
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## (54) METHOD OF CLEANING SEMICONDUCTOR WAFER

## (57)Abstract:

PURPOSE: To make the high clean surface of a wafer, where adherent foreign matters are extremely few and besides there is no problem of metallic pollution, by cleaning the natural oxide film being made on a semiconductor wafer in an SC1 cleaning process, leaving only the specified thickness in dilute HF cleaning process.

CONSTITUTION: In an SC1 cleaning process, a semiconductor wafer is cleaned, using the mixed liquid consisting of aqueous ammonia, hydrogen peroxide water, and pure water, as cleaning liquid. A silicon natural oxide film 1.1-1.2nm thick is made on the surface of the semiconductor wafer. In dilute HF cleaning process 12, the cleaning is performed using the dilute cleaning liquid where the concentration of hydrofluoric acid is about 5%, in short, containing 1:99 fluoric acid. In the cleaning using this dilute HF cleaning liquid, the etching rate to the silicon oxide film is 3nm/min., and the natural oxide film being made on the surface of the semiconductor wafer in SC1 cleaning process can be left in thickness of 0.8nm by performing the cleaning work for only 10 sec.



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## CLAIMS

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### [Claim(s)]

[Claim 1] The washing approach of a semi-conductor wafer of having the rare HF washing process which only the thickness of 0.5-1.0nm leaves the natural oxidation film formed in said semi-conductor wafer at said SC1 washing process by making into a penetrant remover SC1 washing process which washes a semi-conductor wafer by making the mixed liquor of aqueous ammonia, hydrogen peroxide solution, and pure water into a penetrant remover, and the fluoric acid solution around 0.5%, and washes said semi-conductor wafer.

[Claim 2] The washing approach of a semi-conductor wafer according to claim 1 of performing said SC1 washing process and said HF washing process after performing dark HF washing which washes said semi-conductor wafer by making the fluoric acid solution of about 2.5 - 10% of concentration into a penetrant remover.

DETAILED DESCRIPTION

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## [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the washing approach of the semi-conductor wafer applied to the epitaxial layer growth process at the time of manufacturing a semi-conductor wafer, an oxide-film formation process, the diffusion process of an impurity, etc.

[0002]

[Description of the Prior Art] As a washing technique currently used standardly conventionally, there is RCA washing as pretreatment of the production process of semi-conductor wafers, such as an epitaxial layer growth process, an oxide-film formation process, and a diffusion process of an impurity.

[0003] In this RCA washing, it is aqueous ammonia ( $\text{NH}_4\text{OH}$ ). SC1 washing and the hydrochloric acid ( $\text{HCl}$ ) which make a penetrant remover the mixed liquor of hydrogen peroxide solution ( $\text{H}_2\text{O}_2$ ) and pure water ( $\text{H}_2\text{O}$ ) There are SC2 washing which makes a penetrant remover the mixed liquor of hydrogen peroxide solution and pure water, and HF washing which makes a fluoric acid water solution ( $\text{HF}$ ) a penetrant remover.

[0004] The washing approach currently standardly used as pretreatment of the semi-conductor wafer in the process mentioned above is performing rare HF washing which makes a penetrant remover the fluoric acid solution of about 0.5% of concentration about 1 minute, after performing SC1 washing.

[0005] Moreover, when removing a pad oxide film like gate oxide, exposing a silicon substrate and newly forming silicon oxide, after performing SC1 washing, dark HF washing which makes a penetrant remover the fluoric acid solution of about 2.5 - 10% of concentration is performed.

[0006]

[Problem(s) to be Solved by the Invention] By the way, this invention person considered the washing approach of a semi-conductor wafer. The following is the technique examined by this invention person, and the outline is as follows.

[0007] That is, although it is effective for removing a wafer adhesion foreign matter, i.e., particle, since SC1 washing has the capacity etched while oxidizing a wafer front face, metal contamination remains that it is hard to remove Fe, Zn, etc. Then, in order to remove this metal contamination, HF washing is performed, and as pretreatment of said semi-conductor wafers, such as an epitaxial growth process, SC1 washing and rare HF washing are usually performed.

[0008] The thickness of the silicon natural oxidation film formed by SC1 washing is stable, and it is 1.1nm - 1.2nm. On the other hand, the etching rates to the silicon oxide of the fluoric acid concentration around 0.5%, i.e., rare HF washing of 1:99 fluoric acid, are about 3 nm/min at a room temperature. The standard processing time of rare HF washing after SC1 washing is about 1 minute from the object which removes removing said natural oxidation film and metal contamination.

[0009] However, if silicon oxide is removed by HF washing and a wafer front face becomes unreserved, since a silicon front face will be activated chemically, a foreign matter becomes easy to adhere. Moreover, by deleting silicon oxide by HF washing, colloidal silica will arise, this will adhere to a wafer, and a foreign matter will increase. It can delete especially

and this is remarkable in dark HF washing with many amounts.

[0010] Moreover, although it was satisfactory about metal contamination conventionally as were mentioned above, and it mentioned above, although dark HF washing was carried out to the degree of SC1 washing as front washing when a pad oxide film was removed like gate oxide, a silicon substrate was exposed and silicon oxide was newly formed, there were dramatically many wafer adhesion foreign matters.

[0011] On the other hand, although an adhesion foreign matter will be reduced if SC1 washing is performed after performing dark HF washing processing in order to reduce this affix, metal contamination poses a problem shortly by the reason too mentioned above.

[0012] The object of this invention solves the trouble mentioned above, and an adhesion foreign matter is to offer the washing technique which makes the wafer front face of the high cleanliness which the problem of metal contamination does not have very few, either.

[0013] The other objects and the new description will become clear from description and the accompanying drawing of this description along [ said ] this invention.

[0014]

[Means for Solving the Problem] It will be as follows if the outline of a typical thing is briefly explained among invention indicated in this application.

[0015] That is, the washing approach of the semi-conductor wafer of this invention has SC1 washing process which makes a penetrant remover the mixed liquor of aqueous ammonia, hydrogen peroxide solution, and pure water, and the rare HF washing process which makes a penetrant remover the fluoric acid solution around 0.5%, and leaves and washes only 0.8nm only of thickness of 0.5-1.0nm for the natural oxidation film formed in the semi-conductor wafer at SC1 washing process preferably at a rare HF washing process.

[0016]

[Function] If it was in the washing approach of the semi-conductor wafer of this invention of having said washing process, since only thickness predetermined at a rare HF washing process left the natural oxidation film formed in the front face of a semi-conductor wafer at SC1 washing process, the front face of a semi-conductor wafer is covered with the natural oxidation film, and serves as the hydrophilic property of a stable condition chemically, and a foreign matter stops being able to adhere easily. Moreover, the metal contamination which remains at SC1 washing process is removable by removing the natural oxidation film thinly in HF washing process.

[0017]

[Example] Hereafter, the example of this invention is explained to a detail based on a drawing.

[0018] (Example 1) Drawing 1 (a) is process drawing showing the washing approach of the semi-conductor wafer which is one example of this invention, and it has SC1 washing process 11 and the rare HF washing process 12 so that this invention may be illustrated.

[0019] At this SC1 washing process 11, washing to a semi-conductor wafer is performed by making the mixed liquor of aqueous ammonia, hydrogen peroxide solution, and pure water into a penetrant remover. A penetrant remover is heated by about 75-85 degrees C, and performs the predetermined processing time and processing-time washing of an about [ usual 10-20 minute ]. In this SC1 washing process, the silicon natural oxidation film of 1.1-1.2nm thickness is formed in the front face of a semi-conductor wafer.

[0020] At the rare HF washing process 12, washing is performed using the rare HF penetrant remover of about 0.5% of fluoric acid, i.e., 1:99 fluoric-acid concentration. By

washing using this rare HF penetrant remover, although it is 3 nm/min at a room temperature and washing was made for 1 minute in the former, if the etching rate to silicon oxide is in this invention, when for 10 seconds performs washing, it can leave the natural oxidation film formed in the front face of a semi-conductor wafer at SC1 washing process by the thickness of 0.8nm. Thus, the washing sequence of this example is SC1 washing and rare HF washing 10 seconds, and can give a hydrophilic property to the front face of a semi-conductor wafer.

[0021] If the thickness of the natural oxidation film which it leaves at the rare HF washing process 12 is controllable and it leaves the natural oxidation film by adjusting the concentration and the processing time of a rare HF penetrant remover more thinly than said example, when the 1:99 fluoric acid of the same concentration as the above-mentioned will be used for it, it will lengthen the processing time.

[0022] In order to remove the metal contamination which remains the natural oxidation film formed in the front face of a semi-conductor wafer at SC1 washing process on this front face, it may be made to perform rare HF washing processing so that it may consider as the thickness of about 1.0nm. Metal contamination is unremovable unless it carries out rare HF washing to extent in which the thickness of 1.0nm remains.

[0023] On the other hand, when HF washing is performed to extent set to 0.5nm or less in the thickness of the natural oxidation film, the front face of a semi-conductor wafer will be activated chemically, and a foreign matter will adhere on the surface of a wafer. Therefore, the thickness of the natural oxidation film which it leaves at HF washing process is 1.0-0.5nm, and is 0.8nm preferably.

[0024] (Example 2) Drawing 1 (b) is process drawing showing the washing approach of the semi-conductor wafer which are other examples of this invention. This washing approach is applied, in case a putt oxide film is removed like gate oxide, a silicon substrate is exposed and silicon oxide is newly formed.

[0025] In that case, it carries out before SC1 washing process 11 of having mentioned above the dark HF washing process 10 of 2.5 - 10% of fluoric acid concentration, i.e., 1:19 fluoric acid. The processing time of this dark HF washing process 10 is adjusted by the thickness of the oxide film to remove. Therefore, the washing sequence in this example is part [ for the dark HF washing X ], SC1 washing, and rare HF washing 10 seconds. The processing time in this rare HF washing process 12 can also be set as predetermined time amount according to the thickness of the oxide film which it leaves like said example.

[0026] Drawing 2 and drawing 3 are drawings showing the experimental data of the washing approach of the semi-conductor wafer of this invention, and drawing 2 shows the data which measured the level of the adhesion foreign matter (more than phi0.3micrometer) to the wafer when washing a semi-conductor mirror wafer.

[0027] Like before, when rare HF washing processing was performed for 1 minute after SC1 washing, as Sign A showed drawing 2, it was an average of 28 per semi-conductor wafer, but when the washing approach of this invention was enforced, the foreign matter adhering to a semi-conductor wafer decreased sharply with an average of 2.3 pieces.

[0028] Drawing 2 investigates the processing time of rare HF washing after SC1 washing process 11, and the relation of the metal contamination which remains to a wafer by minority carrier life time assessment. Although metal contamination exists when HF processing is not performed after SC1 washing, it turns out in HF processing 5 seconds that life time is recovered.

[0029] Thus, by the conventional washing approach, although hundreds of several 10-foreign matters 0.3 micrometers or more had adhered to the semi-conductor wafer, if particle size is in the example of this invention, it can reduce the number of adhesion of a foreign matter partly to it even at level. And also in reduction \*\*\*\*, the pattern defect of a semiconductor integrated circuit, and the oxide-film defect, adhesion foreign matters decreased in number in this way, and the yield of a semiconductor device improved.

[0030] As mentioned above, although invention made by this invention person was concretely explained based on the example, it cannot be overemphasized that it can change variously in the range which this invention is not limited to said example and does not deviate from the summary.

[0031] For example, although for 10 seconds washed the semi-conductor wafer after SC1 washing using HF penetrant remover of 1:99 fluoric-acid concentration in the example, it may be made to perform HF processing only for 30 seconds using HF penetrant remover of 1:999 fluoric-acid concentration with concentration lower than this. If it leaves preferably 0.5-1.0nm of natural oxidation film formed at SC1 washing process by the thickness of 0.8nm, the concentration and the processing time of fluoric acid can be set as various values.

[0032] Although the above explanation explained the case where it applied in order to wash silicon semi-conductor wafers which are the field of the invention about invention mainly made by this invention person, such as VLSI and LSI, it is not limited to this and this invention can be applied also for washing of semi-conductor wafers, such as GaAs.

[0033]

[Effect of the Invention] It will be as follows if the effectiveness acquired by the typical thing among invention indicated in this application is explained briefly.

[0034] (1) Clearance of an adhesion foreign matter is made by washing semi-conductor wafer SC1, forming the natural oxidation film in a front face.

[0035] (2) By performing HF washing after SC1 washing, the metal contamination which remains on the front face of the semi-conductor wafer after SC1 washing is removable.

[0036] (3) When it also leaves preferably 0.5-1.0nm of about 0.8nm of natural oxidation film in rare HF washing, the front face of a semi-conductor wafer serves as a hydrophilic property, and it is prevented that a foreign matter adheres to a semi-conductor wafer after rare HF washing processing.

[0037] (4) ., therefore the semi-conductor wafer with which an adhesion foreign matter has the front face of the high cleanliness which does not have the problem of metal contamination very few can be obtained.

[0038] (5) Since ., thus an adhesion foreign matter decreased, the pattern defect of a semiconductor integrated circuit and the oxide-film defect decreased, and the yield of a semiconductor device improved.

## DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] (a) and (b) It is process drawing showing the washing process of the washing approach of the semi-conductor wafer of this invention.

[Drawing 2] It is the comparison graph which shows the level of the wafer adhesion foreign matter to the mirror wafer washed using the washing approach of this invention as compared with the conventional washing approach.

[Drawing 3] It is the comparison graph which shows the processing time and life time of HF washing after performing SC1 washing.

[Description of Notations]

10 Dark HF Washing Process

11 SC1 Washing Process

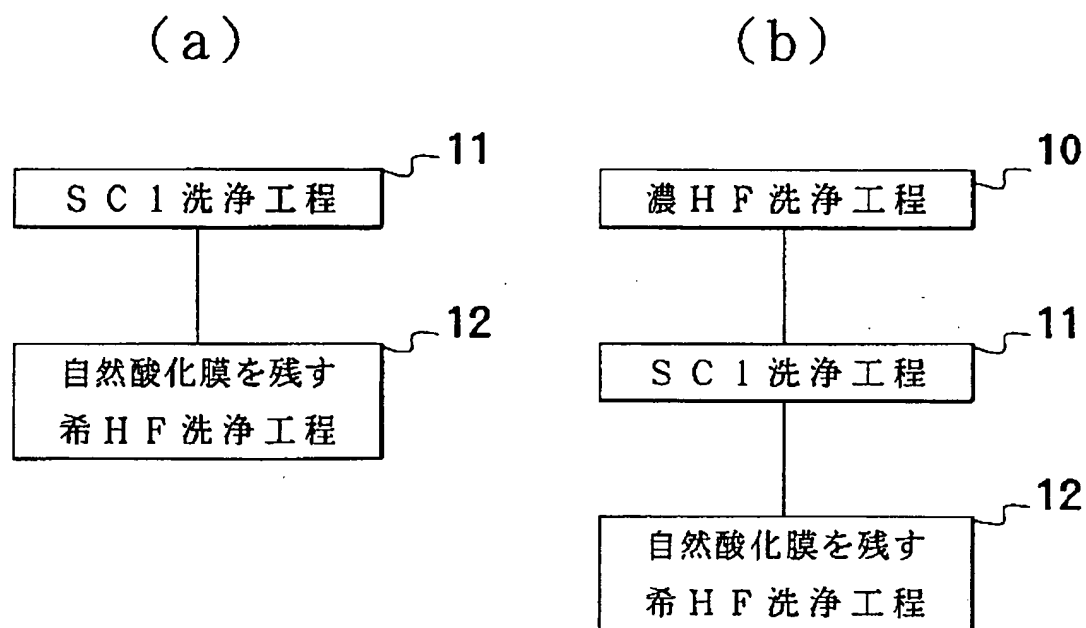
12 Rare HF Washing Process



## DRAWINGS

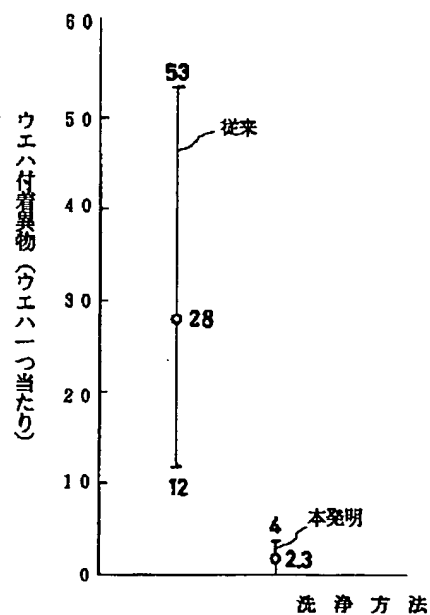
[Drawing 1]

図 1



[Drawing 2]

図 2



[Drawing 3]

図 3

